PB87-176699

Transition-Flow Reactor Tube for Measuring Trace Gas Concentrations

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

1986

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completin

1. REPORT NO.	2.	3. R PB87-176699
EPA/600/J-86/308		

4. TITLE AND SUBTITLE
A Transition-Flow Reactor Tube for Measuring Trace Gas Concentrations (Journal Version)

5. REPORT DATE
1986

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.L. Durham, T.G. Ellestad, L. Stockburger, K.T. Knapp, and L.L. Spiller

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
(Same as Block 12)

10. PROGRAM ELEMENT NO.
CCVN1A/07-4037(FY-85)

11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS
Atmospheric Sciences Research Laboratory-RTP,NC
Office of Research and Development
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES
JAPCA, 36(11):1228-1232, November 1986

16. ABSTRACT

Dry deposition contributes significantly to the acidification of ecosystems. However, difficulties in measuring dry deposition of reactive gases and fine particles make routine direct monitoring impractical. An alternate approach is to use the "concentration monitoring" method in which dry deposition is estimated from the product of measured concentration and estimated deposition velocity. A sampling system that performs over the period of 6 hours to 7 days, depending on atmospheric concentrations, has been developed. It consists of a Teflon cyclone to exclude particles larger than about 2 μm, selective solid adsorption media for reactive gases - some of which are sampled from a transition flow to avoid bias from particle evaporation, a particle filter, and a final gas adsorption filter to collect the remaining trace gas. The sampler is the first reported application of transition flow mass transfer for the collection of trace atmospheric gases. Laboratory and field tests have shown that the sampler performs well for $HNO_{3(g)}$.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	Unclassified	6
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA/600/J-86/308
JOURNAL ARTICLE

TECHNICAL PAPERS

JAPCA 36: 1228-1232 (1986)

A Transition-Flow Reactor Tube for Measuring Trace Gas Concentrations

J. L. Durham, T. G. Ellestad, L. Stockburger, K. T. Knapp, and L. L. Spiller
Atmospheric Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

Dry deposition contributes significantly to the acidification of ecosystems. However, difficulties in measuring dry deposition of reactive gases and fine particles make routine direct monitoring impractical. An alternate approach is to use the "concentration monitoring" method in which dry deposition flux is estimated as the product of measured concentration and estimated deposition velocity. A sampling system that performs over the period of 6 hours to 7 days, depending on atmospheric concentrations, has been developed. It consists of a Teflon cyclone to exclude particles larger than about 2 μm, selective solid adsorption media for reactive gases—some of which are sampled from a transition flow to avoid possible bias from particle evaporation, a particle filter, and a final gas adsorption filter to collect the remaining trace gas. The sampler is the first reported application of transition flow mass transfer for the collection and quantitative measurement of trace atmospheric gases. Laboratory and field tests have shown that the sampler performs well for HNO_3(g).

The assessment of ecosystem acidification and design of effective control strategies require that we monitor the trends, determine the patterns and, in case studies for model validation, measure the air quality and deposition of major acidifying and neutralizing pollutants. These pollutants include the trace gases SO_2, HNO_3, NO_2, H_2O_2, O_3, NH_3 and particulate SO_4^{2-}, NO_3^-, H^+, and NH_4^+. However, monitoring the dry deposition of these species in a regional network poses severe problems, which include our inability to measure directly most of these trace pollutants deposited onto natural surfaces, concern that surrogate surfaces may not simulate the removal action of natural surfaces, and the complexity and demanding instrumentation requirements of micrometeorological methods for direct dry deposition measurement.[1]

Because of the lack of direct dry deposition methods suitable for network monitoring, the National Acid Precipitation Assessment Program (NAPAP)[2] is developing an inferential method[3] that requires concentration monitoring. In this method, the dry deposition flux is estimated as the product of the measured concentration (C) of the pollutant of interest and its estimated velocity of deposition (v_d):

$$\text{Flux} = \overline{v_d C}. \qquad (1)$$

Copyright 1986-Air Pollution Control Association

where the product $\overline{v_d C}$ is averaged over a period of stationary conditions in the atmosphere (generally less than one hour). The term "stationary" means that v_d and C are changing slowly enough that they can be represented by average values. Over nonstationary periods, an estimate of the flux is

$$\langle\text{Flux}\rangle = \overline{v_d}\,\overline{C} \qquad (2)$$

and the error in the estimate is

$$\text{Error} = \text{Flux} - \langle\text{Flux}\rangle = \left[(1/n)\sum_{i}^{n}(\overline{v_d C})_i\right] - \overline{v_d}\,\overline{C} \qquad (3)$$

where i denotes stationary periods of uniform duration. NAPAP plans to monitor routinely for weekly dry deposition estimates (to compare directly with those for wet deposition) and for periods as short as six hours for regional transport field study cases. Since the variables v_d and C may change continuously and independently during a typical day, the error term must be evaluated as a function of sampling duration. That evaluation will permit specification of a sampling protocol selected to control the error of the concentration monitoring estimate of dry flux within desired limits. The candidate air pollutant sampling protocols include (a) continuous operation of one sampler for 7 days; (b) alternating operation of a pair of samplers for 7 days, one during daylight, the other at night; and (c) intermittent operation for 7 days of several cumulative samplers selected by a real-time measurement of atmospheric stability.

To investigate the error given by Equation 3 for the above sampling protocols, we have developed a modular sampler that possesses these desired attributes:

1. Measure the mean concentration of HNO_3 in the presence of 0.5 μg m^{-3} particulate NO_3^- for durations of 7 days with a precision of ±20 percent for mean concentration ≥ 0.3 μg m^{-3}, and for 6 hours with a precision of ±20 percent for mean concentrations ≥ 3 μg m^{-3}. (The errors in estimating the deposition velocities will be 2–3 times greater and will dominate the errors in estimating dry fluxes.)
2. Contain no hazardous chemicals and be sufficiently rugged to be sent to field sites and returned by postal service. Solid adsorbers are preferred.
3. No specialized personnel required to operate sampler. (No sample changes in field; field operations consist of connecting sampler to air-flow lines and adjusting the mass-flow controller; all sampler maintenance performed by a central laboratory.)

4. End-point detection should be the same as for wet deposition samples (e.g., ion chromatography for SO_4^{2-} and NO_3^-, specific ion electrode for NH_3 and NH_4^+).

The attributes for a sampler for the NAPAP trends monitoring network are expected to include those above, with consideration also given to the costs of equipment, chemical analysis, and skilled personnel.

Sampler Description

The concentrations of reactive gases such as HNO_3, NH_3, O_3, and H_2O_2 may unintentionally be reduced by passing over particles collected on a filter. Also, for the air passing the filter, particle evaporation may increase the concentrations of some gases, especially in the case of the decomposition of NH_4NO_3:

$$NH_4NO_3(s) \rightleftharpoons HNO_3(g) + NH_3(g). \quad (4)$$

Our approach to sampling such gases to avoid these biases is to collect a fraction on a reactive tube wall in transition flow ($2100 < Re < 3500$), taking advantage of the relatively high diffusive flux of a reactive gas compared to that of particles with diameter greater than 0.001 μm. For our sampler, transition flow ($Re = 2600$) was chosen over laminar flow because it exhibits a high but stable gas transfer coefficient to the wall, permits sampling of multiple trace gases, and permits sampling of more air for ancillary particle collection than laminar flow samplers. The use of a single transition-flow reactor (TFR) tube for sampling multiple species costs less and eliminates possible flow rate biases among the species. The stagnant air layer (film) at the wall impedes Brownian deposition of particles.

As an example of the TFR sampler, the mass flux of $HNO_3(g)$ to a Nylon lining can be expressed in terms of a fictitious stagnant air film at the wall and the flow of a turbulent air core passing through the tube.[4] Molecular diffusion through the stagnant film controls the mass transfer to the lining (nylon), and the depletion of the trace reactive gas (HNO_3) as a function of travel distance through the tube is given by the material balance

$$-QdC(x) = F_w dA(x) \quad (5)$$

where $dC(x)$ = the change in the average concentration in the turbulent core,
x = the distance from the start of the active lining,
F_w = the mass flux to the lining,
$dA(x)$ = the axial surface area increment, and
Q = the volumetric flow rate.

The radial mass flux from the turbulent core across the stagnant film to the active lining is

$$F_w = D[\Delta C(r)/\Delta r]. \quad (6)$$

$$= D[C(x) - C_w]/\lambda \quad (7)$$

where C_w is the concentration of the reactive trace gas at the wall of the TFR, and λ is the thickness of the fictitious stagnant film. The concentration of the reactive gas is zero at the surface of the active lining, so Equation 5 becomes

$$-dC(x) = D[C(x)/\lambda]2\pi r Q^{-1} dx. \quad (8)$$

Integrating Equation 8 gives the fraction of reactive gas penetrating the tube past the active lining:

$$C(x)/C(0) = \exp(-2\pi r D x \lambda^{-1} Q^{-1}). \quad (9)$$

The fraction of reactive trace gas deposited is

$$M = 1 - [C(x)/C(0)]$$
$$= 1 - \exp(-2\pi r D x \lambda^{-1} Q^{-1})$$
$$M = 1 - \exp(-2\pi a x/Q). \quad (10)$$

where $a = rD/\lambda$. Thus, the fraction of reactive gas deposited to the active lining depends on the diffusion coefficient, radius of the lined section, stagnant film thickness, flow rate, and length of the lined section.

In practical applications, the TFR sampler must be experimentally calibrated to determine the parameter a at the desired operating transition flow rate Q and active lining length x. The variable λ cannot be measured directly or calculated from theory, since it does not represent a sharp boundary. However, if r and D are known, an effective value of λ can be inferred from the experimental determination of a.

The variation of M due to variation in temperature (T) is small, and that due to variation in pressure (P) is probably small. The diffusion coefficient depends on $T^{1.5}P^{-1}$ (Wilke and Lee[5]), whereas the volumetric flow rate through the mass flow controller depends on TP^{-1}. Since these parameters occur as a ratio in Equation 10, the dependence on pressure cancels, leaving a square root dependence on the ratio of absolute temperatures in the exponential function; however, values of λ cannot be measured directly or calculated from theory. The overall dependence of M on T and P can only be determined by experiment. For T, we have performed experiments covering the range 5°C to 32°C; the results are presented in the next section. We have not investigated the pressure dependence.

Formation of gaseous complexes, such as $HNO_3 \cdot nH_2O$, will modify the diffusion coefficient, which may lead to a serious change in the TFR sampler's efficiency. The most likely lower tropospheric species is HNO_3, but it has been shown that the diffusion coefficient does not change as a function of relative humidity over the range of 5 to 95 percent.[6]

The TFR sampler with particle filter is shown in Figure 1. All surfaces contacting the sample stream, except for the nylon liner and filter, are made of TFE Teflon. The cyclone is reported to have a cutpoint of 2.1 μm for unit density particles at a flow rate of 28.3 L min^{-1} at 25°C.[7] Our system is normally run with two identical 16.1 std. L min^{-1} samplers in parallel following the cyclone, with a nominal 1 L min^{-1} sweep out the bottom of the cyclone. The cyclone's inflow is 33 std. L min^{-1}, which by semiempirical cyclone theory[8] reduces the cutpoint to about 1.8 μm for unit density particles.

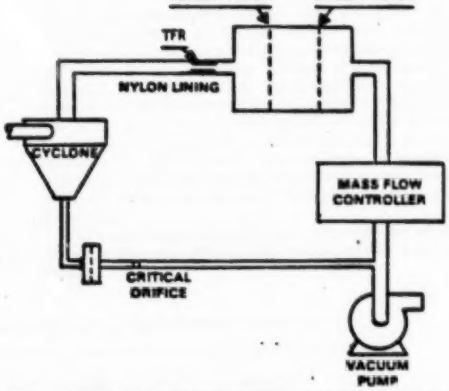

Figure 1. Diagram of the sampler as configured for nitric acid and particulate nitrate measurement. The transition flow reactor (TFR) is the Teflon tube with the nylon liner; it is upstream of the Teflon filter. For the air-HNO_3-particulate NO_3^- system, the TFR collects a constant fraction of the HNO_3. The Teflon filter collects the particulate NO_3^- that does not volatilize. The nylon filter collects the gaseous HNO_3 passing the TFR and Teflon filter and the HNO_3 volatilized from NH_4NO_3 on the Teflon filter.

Table I. Fraction of [HNO_3] collected by the nylon liner (at 20–25°C).

Flow rate (std. L min^{-1})	M, fraction collected	D/λ (cm s^{-1})	λ (μm)	Number of observations
13.4	0.100 ± 0.004	2.76 ± 0.11	435 ± 20	12
16.1	0.089 ± 0.004	2.93 ± 0.14	410 ± 20	10
17.8	0.067 ± 0.008	3.18 ± 0.31	375 ± 40	12

The TFR tube has an inside diameter of 0.95 cm, with a 6 cm distance upstream of the front edge of the first active surface to allow for development of a stable flow profile. We employ an active lining length of 3.2 cm. A stop of slightly smaller inside diameter inside the tube aides in accurate insertion of the lining.

Performance of the TFR Sampler for HNO_3

We experimentally determined the fractional deposition function M for HNO_3(g). For early tests on a prototype TFR sampler (Table I), about 630 μg of nitric acid in solution (heated to aid vaporization) were injected upstream of the nylon-lined section, and the fraction deposited determined through chemical analysis of the mass of nitrate on the nylon lining and the nylon filter. The results in Table I show that the nylon lining removes a constant fraction of the HNO_3(g) entering the nylon-lined section at constant flow rate.

The HNO_3(g) fraction deposited in the TFR is a function of the flow rate, decreasing about 1 percent for a 2 percent increase in flow rate. Estimates of D/λ, the mass transfer coefficient, from Equation 10 are given in Table I. These values increase as flow rate increases, indicating that the stagnant film thickness λ decreases, since D is constant. For a diffusion coefficient of 0.118 $cm^2\ s^{-1}$ for HNO_3, estimates of λ are given in Table I.[6] This thickness of the stagnant film is effective in eliminating particle deposition by Brownian diffusion; for particles with diameter greater than 0.001 μm, theory predicts that less than 0.2 percent is deposited on the nylon liner due to diffusion through the film at the flow rate used. This prediction was confirmed by experiment in which we nebulized a dilute solution of $(NH_4)_2SO_4$ with a DeVilbiss No. 40 nebulizer, producing a size distribution of MMD = 0.4 μm and σ_g = 1.8 (Mercer *et al.*[9]). The ratio of sulfate ion mass found on the liner to the total passing through the tube was about 0.2 percent.

The current version of the concentration monitor was subjected to trials reported in Tables II and III. HNO_3, diffused out of a glass tube from a HNO_3-H_2SO_4 mixture, was bled into a stream of scrubbed test air flowing into the sampler's cyclone. Two TFR tubes followed the cyclone. After exposure, each nylon liner and filter was extracted in 10 mL of eluent and analysed by ion chromatography for NO_3^-. To maximize analytical precision, each filter extract was diluted 1:10 to bring its solution concentration very near that of the corresponding liner's extract. Each sample was analyzed twice in the general order, liner-filter-filter-liner. This ordering helped reduce the effects of slight drift in the IC's response. Note that since M is determined as the ratio of (liner)/(liner + filter), the absolute accuracy of the IC's calibration is irrelevant.

Table II shows the results of four experiments with the dual sampler. For each side, the fraction M is quite stable. The difference between the two sides has been found to be due to imperfect mounting of the tee where the output of the cyclone splits into the two sides. The tee was mounted 0.7 mm off center and was tilted 2 degrees. Though flow rates into each tube were virtually identical (note the excellent agreement of total nitrate for the two sides), the asymmetry apparently caused different turbulence profiles in the two tubes. An alternate dual sampler (with only half the offset and half the tilt) was found to have M = 0.063 ± 0.003 for one side and 0.087 ± 0.006 for the other (three runs). Better construction tolerances should eliminate the difference.

Table II. Determination of M at 24°C and 16.1 std. L min^{-1} (liner, filter, and sum values are $\mu g\ NO_3^-$).

Run No.	Side 1				Side 2			
	Liner	Filter	Sum	M	Liner	Filter	Sum	M
1	23.3	245	269	0.0869	26.0	239	265	0.0982
2	17.1	182	199	0.0860	19.4	178	197	0.0987
3	16.2	171	188	0.0865	18.0	167	185	0.0971
4	19.5	210	229	0.0850	22.1	105	227	0.0973

Table III presents the determination of M at various temperatures and flow rates. The effect of temperature is small and shows the compensating influence of the stagnant film thickness. The effect of flow rate is small also, considering that the variation shown is for a ± 11 percent change in flow rate about 16.1 std. L min^{-1}; a typical mass flow controller maintains the preset flow to within about 2 percent. We conclude that the fraction of trace gas removed by the liner over typical temperatures and using modern mass flow controllers is quite stable and easily meets the precision goal of 20 percent.

HNO_3 and particulate NO_3^- concentrations are obtained from the strip and filters in the concentration monitor as follows:

Table III. Determination of M at various temperatures and flow rates (number of observations in parentheses).

Temperature (°C)	Flow rate (std. L min^{-1})	Side 1	Side 2
5	16.1	0.088 ± 0.005 (4)	0.099 ± 0.006 (4)
24	16.1	0.086 ± 0.001 (4)	0.098 ± 0.001 (4)
29–32	16.1	0.084 ± 0.001 (4)	0.095 ± 0.001 (4)
24	14.3	0.088 ± 0.001 (2)	0.102 ± 0.001 (2)
24	18.0	0.080 ± 0.0004 (3)	0.094 ± 0.0003 (2)

If A = atmospheric HNO_3 concentration
B = atmospheric particulate NO_3^- concentration
X = mass of NO_3^- on nylon liner
Y = mass of NO_3^- on Teflon and nylon filters
M = fraction of HNO_3 removed by nylon liner
g = fraction of particulate NO_3^- unintentionally deposited onto the nylon liner
V = volume of air sampled
k = ratio of molecular weights of NO_3^-/HNO_3 (= 62/63)
then

$$X = MkAV + gBV \quad (11)$$

$$Y = (1 - M)kAV + (1 - g)BV \quad (12)$$

Solving for A and B,

$$A = [X - g(X + Y)][kV(M - g)]^{-1} \quad (13)$$

$$B = (X + Y - kAV)V^{-1} \quad (14)$$

flow tube sampler for HNO_3. This sampler had a 40-cm long Nylon liner, 1 L min^{-1} flow rate, and 1-cm inside diameter. Using the Gormley and Kennedy[10] equation to calculate the fraction removed from laminar flow by the first 5 cm of the liner, we computed the concentration of HNO_3 to be 0.8 ± 0.1 $\mu g\ m^{-3}$, in good agreement with the TFR samplers.

Urban HNO_3 and Particulate NO_3^- TFR Sampling Results

The TFR sampling system was operated for 11 periods for 5 days in August 1983 at the City of Hope National Medical Center, Duarte, California, which is about 2 km southwest of the junction of Interstate Highways 605 and 210. The system was similar to that shown in Figure 1, except two TFR and filter sets were operated from the cyclone as described in the section "Sampler Description." The NO_3^- masses for the nylon strip in the TFR, the Teflon filter, and the nylon filter

Table IV. HNO_3 and NO_3^- data from field experiments.

Start date	Sampler	Total hours	[HNO_3] ($\mu g\ m^{-3}$)	Fine [NO_3^-] ($\mu g\ m^{-3}$)	Site
7/28/83	A	60.1	2.7 ± 0.2	0.3 ± 0.2	Argonne
	B	60.1	3.5 ± 0.3	0.1 ± 0.2	Argonne
8/2/83	A	38.8	3.1 ± 0.3	0.8 ± 0.2	Argonne
	B	38.8	3.3 ± 0.3	0.7 ± 0.2	Argonne
10/22/84	A	95.1	0.7 ± 0.1	0.3 ± 0.1	RTP
	B	95.1	0.8 ± 0.1	0.2 ± 0.1	RTP

The field performance of the prototype concentration monitor was tested at Argonne National Laboratory (ANL) and outside our laboratories at Research Triangle Park (RTP). Data are shown in Table IV. During the sampling at Argonne we operated a modified system, in that the Teflon filter was omitted. (This modification has no effect on sampler performance. The Teflon filter is necessary only to determine particulate mass.) The HNO_3 masses for each of the two parallel runs agree fairly well. The particulate NO_3^- masses are smaller and agree within experimental uncertainties. Results from the RTP run agree well. In addition to the dual TFR samplers at RTP, we simultaneously ran a laminar

are given in Table V. The indicated experimental standard deviations were obtained from random reanalysis of the sample extract by ion chromatography. We estimated the percent deviations for the others to be the average of that population (± 8.7 percent), with the two largest percent deviations being judged as outliers and excluded from the average. The experimental determination of nitrate ion mass in Table V demonstrates that the agreement between Samplers 1 and 2 is well within the estimated analytical error.

The air concentrations of HNO_3 and fine particulate NO_3^- were estimated through Equations 13 and 14. The estimates

Table V. Gaseous HNO_3 and fine particulate nitrate TFR sample measurements (Duarte, California).

Run No.	August 1983 sampling period (start/stop)	Sampler	Nitrate mass[a] Nylon liner, μg	Teflon filter, μg	Nylon filter, μg	Air concentration [HNO_3], $\mu g\ m^{-3}$	Particulate [NO_3^-], $\mu g\ m^{-3}$
1	8/1 1404 PDT/	1	21.3 ± 0.6	7.20 ± 1.37	223 ± 8	39.6 ± 2.4	2.1 ± 2.3
	1945 PDT	2	21.3	6.00	215	39.6 ± 4.0	0.4 ± 4.7
2	8/1 2016 PDT/	1	5.40 ± 0.30	40.4 ± 0.3	73.9 ± 2.7	5.45 ± 0.43	5.45 ± 0.47
	8/2 0631 PDT	2	5.20 ± 0.46	39.1 ± 1.0	76.8 ± 0.4	5.23 ± 0.56	5.79 ± 0.53
3	8/2 1006 PDT/	1	51.0 ± 9.5	12.7 ± 1.6	476 ± 50	67 ± 13	−4 ± 13
	1805 PDT	2	45.5 ± 0.2	10.0 ± 4.1	457 ± 49	60.3 ± 3.1	0.14 ± 6.3
4	8/2 2153 PDT/	1	1.02	22.6	18.7	1.20 ± 0.14	3.46 ± 0.33
	8/3 0621 PDT	2	1.12	18.3	21.3	1.33 ± 0.15	3.14 ± 0.32
5	8/3 0700 PDT/	1	0.01	13.2 ± 1.7	26.7 ± 1.6	>−0.2 ± 0.2	11.3 ± 0.7
	1021 PDT	2	0.01	12.9 ± 2.8	33 ± 10	>−0.2 ± 0.2	12.9 ± 3.0
6	8/3 1049 PDT/	1	22.8 ± 5.1	3.90	325	71 ± 17	27 ± 17
	1411 PDT	2	21.2 ± 3.5	3.30	330	66 ± 12	32 ± 13
7	8/3 1440 PDT/	1	21.2 ± 0.7	4.10	215	62.5 ± 3.8	0.6 ± 5.8
	1815 PDT	2	20.5 ± 0.2	5.50	220	60.5 ± 3.2	3.9 ± 5.6
8	8/3 1845 PDT/	1	5.00	44.6	73.2	3.86 ± 0.40	4.73 ± 0.65
	8/4 0805 PDT	2	4.90	42.8	76.4	3.77 ± 0.40	4.90 ± 0.66
9	8/4 0820 PDT/	1	38.9	10.8	381	47.0 ± 4.8	−0.7 ± 5.5
	1705 PDT	2	37.4	11.4	413	45.1 ± 4.6	4.5 ± 5.6
10	8/4 1720 PDT/	1	10.6	18.7	113	7.22 ± 0.74	1.44 ± 0.89
	8/5 0845 PDT	2	9.88	18.0	111	6.74 ± 0.69	1.73 ± 0.86
11	8/5 0920 PDT/	1	39.0	6.51	391	48.9 ± 5.0	−0.2 ± 5.8
	1745 PDT	2	38.2	4.14	390	48.0 ± 4.9	0.2 ± 5.8

[a] The standard deviations are indicated or taken to be equal to the average value of 8.7 percent.

of $[HNO_3]$ have percent precisions within the range 5.1–23.4 percent with an average value of 10.9 percent, excluding Run 5. For cases in which particulate $[NO_3^-] > [HNO_3]$, the precision for the estimate of particulate $[NO_3^-]$ is < 14 percent; these cases are Runs 2, 4, 5, and 8. In the other cases, $[HNO_3]$/particulate $[NO_3^-] > 2$, and the precision of the estimate of particulate $[NO_3^-]$ is poor. That is expected, for as can be seen in Equation 14, the estimate contains the difference between the $([HNO_3] + [NO_3^-])$ and $[HNO_3]$; thus, when particulate $[NO_3^-]$ is less than $[HNO_3]$, its precision is governed by that for $[HNO_3]$.

The ambient air results indicate that $[HNO_3]$ possesses a strong diurnal cycle with a maximum during the day and minimum during the night. The daytime range of $[HNO_3]$ for these 5 days was 48–68 $\mu g\ m^{-3}$, and the nighttime range was 1.2–5.3 $\mu g\ m^{-3}$ (the morning case, Run 5, was excluded).

The principle of the TFR sampler can be applied to other reactive trace gases in the atmosphere. We are developing the necessary sorbents for NH_3 and particulate NH_4^+. These sorbents can be installed in series with the Nylon surfaces needed for HNO_3/NO_3^- determination, using the same flow system for economy. Surfaces for other reactive species may also be installed, provided that no premature removal occurs upstream of the intended removal point in the reactive tube.

The Duarte, CA field test demonstrated that the precision for the fine particulate $[NO_3^-]$ is poor when $[NO_3^-] < \sim 0.5$ $[HNO_3]$. That feature does not have important consequences in estimating the total inorganic nitrate flux. Since the deposition velocity of HNO_3 is 1–2 cm/s (Huebert and Robert[11]) and of fine particles is 0.1–0.2 cm/s (see review by Hicks[12]), HNO_3 contributes more than about 90 percent to the dry flux of total inorganic nitrate when $[HNO_3] >$ fine particulate $[NO_3^-]$; for such cases, a precise estimate of $[NO_3^-]$ is not required. For the cases in which $[HNO_3] < [NO_3^-]$, the contribution of NO_3^- is > 10 percent and the precision of $[NO_3^-]$ is comparable to that for the estimate of $[HNO_3]$. While the performance of the sampler has been tailored to take advantage of the large difference in the dry deposition velocities of reactive gases and their particulate products, the sampler is not suited for investigation of problems for which precise particulate $[NO_3^-]$ or $[NH_4^+]$ measurements are required for all conditions (e.g., visibility studies).

Conclusions

Laboratory and field tests have shown that the transition-flow concept is satisfactory for measuring the concentrations of reactive trace gases in the atmosphere, overcoming the problem of biases due to reactions with particles collected on filters and to particle evaporation. Development of a sampler based on this concept is complete for sampling HNO_3 and has acceptable errors for application to concentration monitoring for dry deposition flux measurement. The sampler also performs adequately for fine particulate NO_3^- for cases in which fine particulate $[NO_3^-] > \sim 0.5$ $[HNO_3]$. With development of selective surfaces for other reactive species, the method has wider application.

References

1. B. B. Hicks, M. L. Wesely, J. L. Durham, "Critique of Methods to Measure Dry Deposition," U.S. Environmental Protection Agency, Report No. EPA-600/9-80-050; available from NTIS, Report No. PB81-126443, 1980.
2. "Annual Report—1983," National Acid Precipitation Assessment Program, available from: Interagency Task Force on Acid Precipitation, Council on Environmental Quality, Washington, DC (1983).
3. B. B. Hicks, "Measuring dry deposition: re-assessment of the state-of-the-art," *Water, Air, Soil Pollut.*, in press (1986).
4. A. S. Foust, L. A. Wenzel, C. W. Clump, L. Maus, L. B. Andersen, *Principles of Unit Operations*, John Wiley and Sons, New York, 1964, pp. 148–149 and 184–185.
5. C. R. Wilke, C. Y. Lee, "Estimation of diffusion coefficients for gases and vapors," *Ind. Eng. Chem.* 47: 1253 (1955).
6. J. L. Durham, L. Stockburger, "Nitric acid-air diffusion coefficient: experimental determination," *Atmos. Environ.* 20: 559 (1986).
7. W. B. Smith, R. R. Wilson, Jr., D. B. Harris, "A five-stage cyclone system for in situ sampling," *Environ. Sci. Technol.* 13: 1387 (1979).
8. N. A. Fuchs, *The Mechanics of Aerosols*, Pergamon Press, New York, 1964, pp. 126–139.
9. T. T. Mercer, M. I. Tilley, H. Y. Chow, "Operating characteristics of some compressed air nebulizers," *Am. Ind. Hyg. Assoc. J.* 29: 66 (1968).
10. P. Gormley, M. Kennedy, "Diffusion from a steam flowing through a cylindrical tube," *Proc. R. Ir. Acad.* 52A: 163 (1949).
11. B. J. Huebert, C. H. Robert, "The dry deposition of nitric acid to grass," *J. Geophys. Res.* 90: 2085 (1985).
12. B. B. Hicks, "Dry Deposition Processes," in *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers*, vol. I, A. P. Altshuller, ed., U.S. Environmental Protection Agency, EPA-600/8-83-016AF, 1984.

J. L. Durham, T. G. Ellestad, L. Stockburger, K. T. Knapp, and L. L. Spiller are with the Atmospheric Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

Any policy issues discussed herein should not be construed to represent official Agency policy. Mention of trade names or commercial products is for information only and does not constitute endorsement or recommendation for use.

Submitted to *JAPCA* for peer review February 6, 1986; the revised manuscript was received August 11, 1986.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.